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PHYSICO CHEMICAL CHARACTERISTICS OF PAPER MILL EFFLUENTS AND ITS TREATMENT PROCESS

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Abstract

Paper mills need high purity water to get pure cellulose, high bright paper, caustic and lime. The proportion of water to chemicals and fibers is indicated by solid percentage and consistency. The process involved are debarking, chipping of woods, wet piling of bagasse, cooking, washing, screening, cleaning, dewatering and bleaching in pulp making, stock proportioning, cleaning, screening, sheet forming, drying and broke handling in paper making and evaporation of black liquor, combustion of black liquor in recovery boilers, causticizing in soda recovery process. In each stage of pulp and paper process large amount of effluents are generated and their physico-chemical properties are varied in the presence of organics and inorganics. The effluent generated have high dissolved solids, high COD and BOD, dark brown color with varied pH range and it affects the aquatic environments. In the presence study is mainly focused on characterization of a paper mill effluent and treated with three different adsorbents such as with alum, charcoal, fly ash and neutral sodium silicate. The study shows that the treated effluent have good reduction in total solids, total dissolved solids, total organics, COD, BOD and results in colorless effluent.

Keywords: *Pulp; Paper; Soda recovery; Effluent; fly ash; sodium silicate; charcoal; COD; BOD.*

1. INTRODUCTION:

The paper mill requires a large volume of water for the process of pulping, paper making, chemicals recovery and boiler operations. Water is used in all the unit operations of pulp and paper making processes such as in chemical preparation plant, pulp dilution, centri cleaning, felt cleaning shower, wire section high pressure shower, couch press roll lubrication tower, felt lubrication shower, pickup roll lubrication, breast roll shower, broke pit showers, couch pit showers, thickner showers, refiner gland cooling, compression cooling, pump gland cooling, rewinder drum cooling, paper reel cooling and floor washing. Blow heat recovery system, brown stock washing, bleaching, washing, bleach chemical preparation, decker Thickner shower, pulp dilution, pulp gland cooling and Floor cleaning in pulping section. Water is also used in used in Demineralization plant and scrubber in boiler house [1-3] . In pulp mill cellulose is obtained by removing lignin from wood by cooking process using sodium hydroxide, sodium sulfide as the active alkali [4] .The extended delignification is done with molecular oxygen at alkaline pH and Chlorine dioxide in acidic pH. The elemental chlorine generated during oxidation of lignin is responsible for the formation of AOX.[5-6]. The washed spent liquor obtained during cooking and washing process contains mainly dissolved organics residues, lignin and carbohydrate and degradation products as main components and inorganic components like sodium hydroxide, sodium carbonate and organically bound sodium. The organics are burnt in recovery boiler to produce steam.

The inorganics are recovered as smelt during combustion of black liquor in the recovery boiler which mainly consists of sodium carbonate and sodium sulphide. During causticizing sodium carbonate reacts with calcium hydroxide and gives sodium hydroxide and calcium carbonate. Calcium carbonate is calcined to give calcium oxide. In paper machine the cellulose is refined and mixed with various chemicals like alkyl ketene dimmers, poly aluminum chloride, Retention drainage agents, Anionic trash catchers, silica, brightening agents, defoamers, dyes, fillers and pigment soups to give required properties of paper. Excess chemicals always

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let out in waste water. In water treatment plant sodium chloride is used to regenerate the softener, the back wash will have high sodium as well as inorganic and total dissolved solids which will be drained.

Wash water/filtrates which are not used further in process are discharged into the effluent. The discharges in chemical bagasse pulp plants are bagasse wash water, pith wash water, boom stacker wash water, leakage of wash water from reclaim chest, collection tank, stone catch tank, leakages from cooling glands, spillage of weak black liquors at brown stock washing or twin roll press. Drainage water from aqua separators, screw press, rejects from alkaline filters, acid filters, EOP filtrate chest overflow and acid used to wash screens to remove dirt and scales are drained. The discharges in hard wood pulp plants are wash water from chip washing system, leakages from tanks, lines, glands, chest overflows, spillage of cooking liquor, coarse and fine rejects, disposal of black liquor pit cleaning and the drains from scrubbers, acid liquid filter, DHT filtrate chests. Discharges from soda recovery plants are leakage of black liquor during screening, spillage of weak and heavy black liquors, generation of contaminated water during evaporator tube cleaning, spillage of salt cake, furnace oil, leakage of feed water and drain from vacuum seal pit, foul condensate, spillage of lime stone, lime kiln bearing cooling water, leakages from lime mud lines, caustic handling line, drug mud tank overflow and drains from lime mud filters and dreg filter condenser. Discharges from power boiler plants are spray water in coal handling, condensate hot well overflow and boiler blow down. The discharges from water treatment plants are the generation of acidic effluent and alkaline effluent during DM plant operation, waste water in reverse osmosis process, wash water of sand filter, activated carbon filter and leakages of acids during storage.

The discharges form chemical additive plant and color coating kitchen are spillage of calcium carbonate, starch, pigment chemicals and the wash water due to tank cleaning. The discharges from paper machine plants are leakages from caustic and biocide tank, pulp leakage from all pumps and agitator glands, cooling water leakage from all pumps and agitators, vacuum pump sealing water, overflow from broke tower, felt uhle box, cloudy and clear chests and the rejects of centri cleaner, centri screen, high density cleaner, algas filter, speed sizer starch filter, multi sorter and mini sorters are drained. The discharges from chlorine dioxide plants are hypo leakages, hydro chloric acid spillage, chlorine dioxide spillage, back flushing of VAM machine, strong chlorate filter spillage of chlorate and brine solution and the effluent generated during HCL unit washing, heat exchanger acid washing and strong chlorate filter acid washing.

The paper mill waste water contains color, very high biochemical oxygen demand, chemical oxygen demand due to presence of lignin and its derivatives, chlorinated compounds, suspended solids, fatty acids, tannins, resins acids, sulfur and its compounds. Lignin and its derivatives show high stability to degradation. Secondary biological treatment is not effective in reducing color. The substances discharged show a tendency to bio accumulate in fish and other aquatic organisms, they may cause chronic toxicity or interfere with reproduction, gives bad taste or odor, stimulate algal growth and thereby cause eutrophication and have genotoxic and other chronic toxic properties and harmful to agricultural crops, aquatic life and human beings [7-8]. So, it is important to remove all toxins from the paper mill effluents before discharge into the environment [9-12]. In the present investigation mainly focused on physico-chemical characterization of the paper mill effluents collected from various unit operations followed by adsorption process using three different adsorbents for the removal contaminants from the effluent.

2.0 MATERIALS AND METHODS

Alum, Na_2SiO_3, NaOH and H_2SO_4 were received from S.D. Fine Chemicals (Pvt), India Ltd, Chennai. Fly ash from low UBC boiler (collected from pulp and paper industry) was utilized. Wood barks were collected locally from Eucalyptus, Neem and Causarina trees and processed.

2.1 Preparation of activated carbons from wood barks

Wood barks were cut into small pieces and washed with water to remove dirt and sand. The wood bark materials were loaded in a furnace heated to 800^0 C under inert atmosphere for 4 hrs. Then carbon materials were activated chemically using calcium carbonate, sieved into different fractions and stored in a air tight container for further use. The activated carbons were characterized for its ash content, moisture, calorific values and fixed carbon content.

2.2 Collection of Waste water sample and characterization

Wastewater samples were collected and characterized as per standard method from different unit operations from the paper industry as given below: bagasse wash water (high BOD stream); Bagasse pulp plant filtrate/discharges; Hard wood

pulp plant filtrates and discharges; Soda recovery plant discharges; Paper machine plant discharges; ClO_2, WTP, CAP and effluent treatment plant samples.

3.0 RESUTS AND DISCUSSION

3.1 Physico-chemical characteristics of bagasse wash water (high BOD stream):

Bagasse, non-wood fiber, dries depithed and stored by wet bulk storage method for annual requirements. Boom stacker is used to make slurry of bagasse with water and to store on open bagasse yard. The excess water drained out will have high BOD/COD. During storage bagasse soften and release adhered pith. Pith is removed during washing. Pith wash water will have high dissolved sugars. Bagasse is washed and cleaned by passing the slurry with 1.5% consistency through reclaim chest, destoner and sand riffler. The water is removed in aqua separators. The bagasse feed to digesters will have 35% consistency. The remaining 65% of wash water will have acidic pH and dissolved sugars. The characterization of bagasse wash water which has high BOD 3214 -6900 mg/l is given in figure 1.

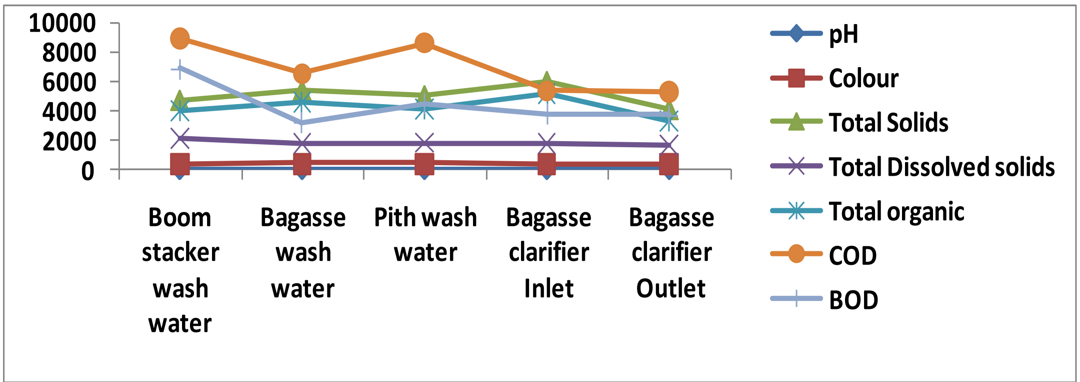

Fig. 1: Physico-chemical characteristics of bagasse wash water (high BOD stream)

3.2 Physico-chemical characteristics of hard wood pulp plant filtrates and discharges:

Hard wood plant has cooking, oxyzen delignification and DHT-EOP-D_1 bleaching stages for lignin removal. In oxyzen delignification oxydized white liquor is added in two stages, high pressure at low temperature and low pressure at high temperature. In DHT stage ClO_2 and sulphuric acid added to pulp at pH 1.8 to 2.3 pH at 90ºC, in EOP stage NaOH, H_2O_2 added to pulp at pH 10-12 and at tempearature 85ºC, In D_1 stage ClO_2, NaOH, H_2SO_4 is added to pulp at pH 4.0-5.0. SO_2 is added to consume residual ClO_2. The resulting filtrates have acidic and alkaline nature as shown in figure 2.

Hardwood pulp plant discharges/filtrates have the pH in the range from 2.2 to 9.4, conductivity 5524-22275µmhos/cm and color 134-29000 pt.co.units. The total dissolved solids varied from 3512 to 11360 ppm are higher than total suspended solids from 402 to 10994 ppm. The total inorganics were estimated 1512 to 10500 ppm and it was higher than total organics 1770-11854 ppm upto EOP stage, in D_1 stage and hard wood final outlet have higher organic solids 2402-2938 ppm than inorganic solids 1512-1802 ppm. The hardwood plant discharges/filtrates have COD level of 1296 to 10592mg/l and BOD from 678to 5606mg/l.

The DHT filtrates are drained into effluent channel, all other filtrates are recycled. Total dissolved solids and suspended solids have gradual reduction throughout the bleaching sequence. Alkaline bleaching has higher color values. Acidic filtrate of DHT and D_1 have less pollution load than hardwood final discharge shows some discharge are from delignification stages by leakage, overflow are by floor cleaning.

The chemical bagasse plant has acidic pH in Do and D1 stage 4.3 and 4.6, 6.8 and 6.1 in EOP and bagasse plant outlet. The colur values are 5800,900,950,260 and1900 pt.co.units, total dissolved solids values are 7024, 5484, 4228, 3812, and 4068 ppm, total suspended solids values are

2892,2376,3814,4294 and 1940 ppm, the total inorganics are 3222,3136,2264,2184,2234 ppm, the total organics are 6694,4724,5778,5922 and 3774 ppm and the BOD values are 3901,2400,2042,2940 and 1808 mg/l in pre thickner, Do, EOP, D1 and bagasse plant outlet discharges.

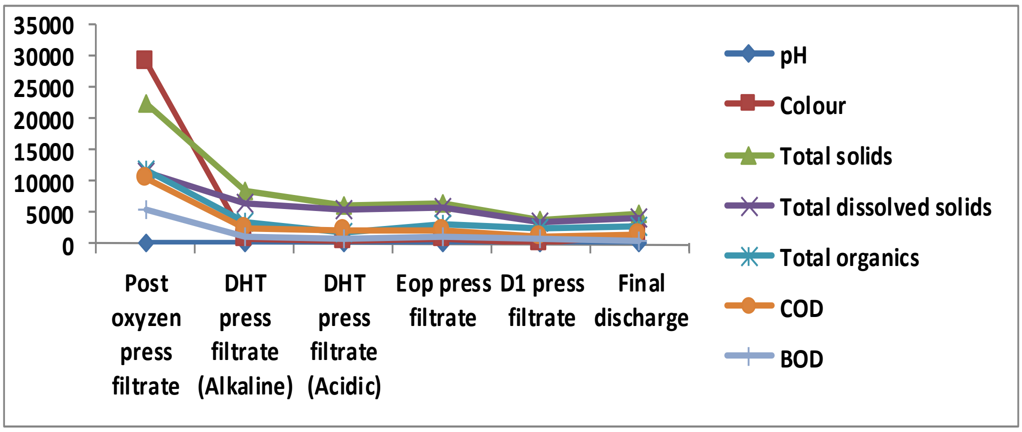

Fig. 2: Physico-chemical characteristics of hard wood pulp plant filtrates and discharges

3.3 Physico-chemical characteristics of paper machine plant discharges:

Centri cleaner rejects:

Thick stock obtained from the stock regulating box mixed with silo water at primary fan pump and feeded to the primary centri cleaner. The centri cleaners separate fiber and heavy particles on the basis of difference in settling velocities. The rejects are feed to the secondary, tertiary and quaternary cleaners and remaining accepts are counter currently feeded. Quaternary cleaner rejects are drained. The rejects contain high concentration of fibers and grit and sand.

Centri screen rejects:

After deaeration pulp is feeded into the primary screen through secondary fan pump. Screen separate foreign materials from fibers which differ from size and shape. Screen have cylindrical outer frame and inner slotted basket. The size of the slotter will be 0.1 to 0.4mm. The lesser size fiber and fillers passed through the slits and discharges as accepts. The substances which are bigger than 0.4mm discharge as rejects. The secondary screen rejects are drained.

Cloudy and clear chest overflow:

Pulp from couch pit, press pit and silo overflow are collected in excess white water chest and the fibers are recovered in save all as mat and the filtered white water stored in cloudy and clear chest which have 400 ppm and 200 ppm of TSS as maximum.

Broke high density cleaner rejects:

The pulp from trim pulper, press pit, under the machine pulper, finishing house pulper are stored in broke tower and broke is added to the furnish after high density cleaning. The rejects are drained.

Size press effluent:

The starch and optical brightening agents are coated in size press. Enzyme is added to maintain viscosity. The starch is continuously filtered and used. Filter wash water are drained. The paper machine discharges have neutral and alkaline pH due to alkaline sizing as shown in fig.3. The pH values are 7.1 to 7.9. The color values are very less for example, 20 to 60 pt.co.units. It has very less sodium concentration, which fit in the pulp mill dilution. The COD values were high due to high discharge of 4% in broke from high density cleaner rejects where as all other discharges have 0.01 to 1.2% consistency. The flow of broke high density cleaner discharge is very less 45m^3/day whereas all other discharges have 144-2000m3/day. The centri cleaner rejects have high TSS and high inorganic 6706 ppm and 4500 ppm, centri screen rejects have high total suspended solids and

high total inorganic 31730 ppm and 23666 ppm, broke high density cleaner rejects have high total suspended solids and total organics 43520 and 39740 ppm. The CaO values are high in paper machine plant than soda recovery plant due to the usage of calcium carbonate as fillers. If the chemicals are not properly retained by retention aids the paper machine effluent load will be increased.

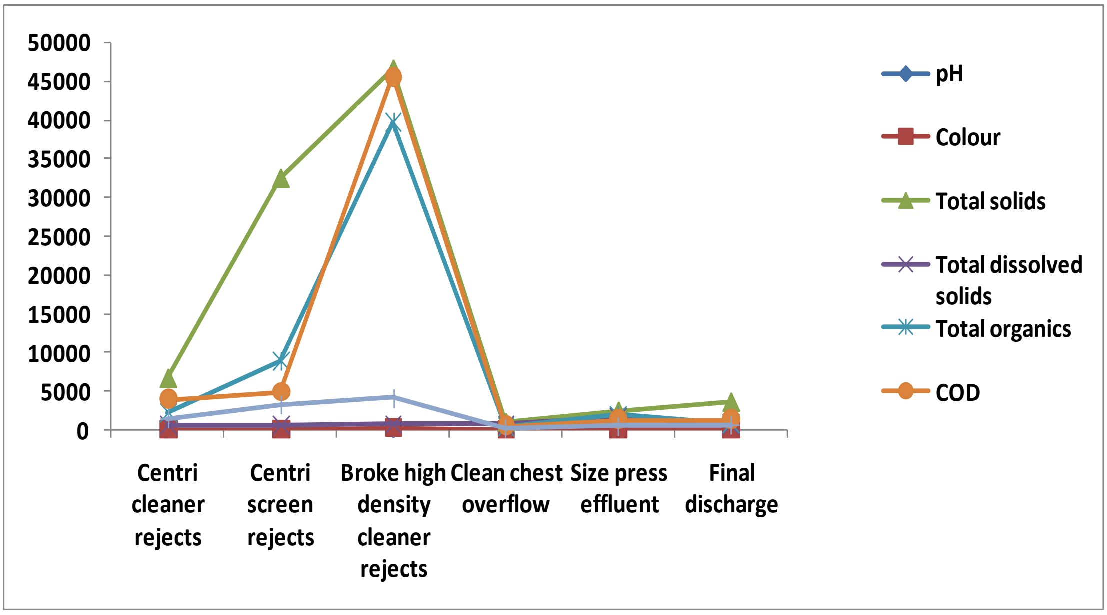

Fig. 3: Physico-chemical characteristics of paper machine plant discharges

3.4 Physico-chemical properties of ClO_2, WTP, CAP and effluent treatment plant samples:

The entire waste water from paper mill is let in two streams. Which have high BOD and low volume stream, low BOD and high volume stream. High BOD effluents are treated in bio-methanisation reactors and anaerobic lagoons and the outlets is clarified in primary clarifiers. Low BOD effluents are passed through bar screens, detritor and grit washing system and feeded in primary clarifiers.The BOD values of clarifiers 1,2 and 3 are 379,589 and 393 mg/l as shown in fig.4.

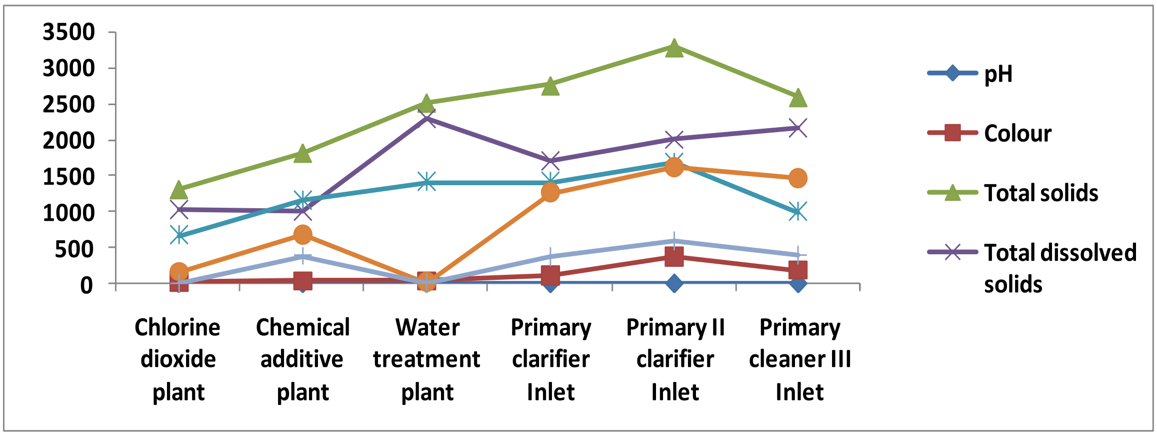

Fig. 4: Physico-chemical properties of ClO2, WTP, CAP and effluent treatment plant samples

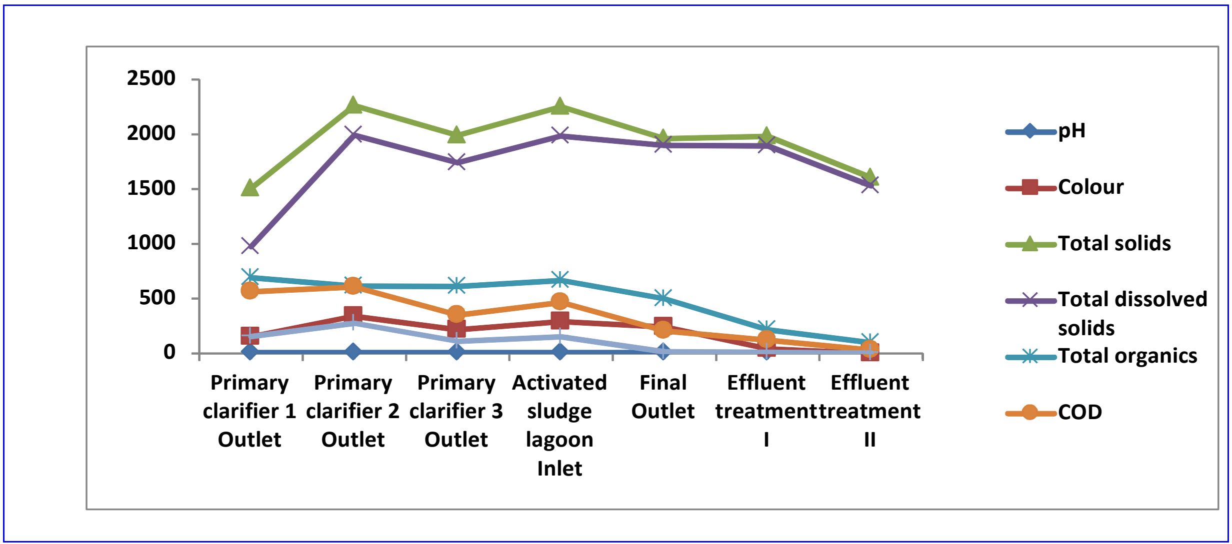

Fig. 5: Treatment of composite effluent its physico-chemical characterization

Table 1. Physcio-chemical characterization of composite final effleunet and adsorption treatment by adsorbents

Properties	Unit	Final mill Outlet	Treatment I	Treatment II
pH		8.2	7.6	6.2
Conductivity	µmhos/cm	3564	3475	2851
Colour	pt.co.units	240	40	BDL
Total solids	ppm	1960	1982	1604
Total dissolved solids	ppm	1900	1894	1528
Suspended solids	ppm	60	88	76
Total inorganic solids	ppm	1462	1766	1506
Total organic solids	ppm	498	216	98
COD	mg/l	205	120	31
BOD	mg/l	14	11	2
Total Hardness	ppm as $CaCO_3$	640	604	580
CaO	ppm as CaO	286	288	255
MgO	ppm as CaO	150	122	94
Chloride	ppm as Cl	426	388	376
Sodium	mg/l	328	320	260
Potassium	mg/l	48	47	45

The outlet from primary clarifiers 1,2 and 3 has BOD values 155,274 and 110 mg/l as shown in fig.5.The reduced values shows the efficiency of clarifiers in settleable solids removal. The primary clarifiers overflow taken to activated sludge lagoon (ASL). The outlet of ASL taken to secondary clarifiers. Secondary clarifier out let was final mill outlet which have BOD values 14 mg/l and the treated effluent is pumped for land irrigation.

3.5 Characteristics of the adsorbents: Fly ash and wood bark activated carbon

The fly ash was characterized for its physico-chemical properties. The unburnt carbon is ranged from 5-12%, ash content is 88-95% and the calorific values was observed from 600 to 900 kilocalories/kg. Activated carbon from Eucalyptus, Neem and causarina wood bark has moisture values are ranged from 2.0%, 2.1%, and 2.2% respectively. Ash values are 16.8%, 7.4%, 4.5%, Volatiles are 47.9%, 43.2%, 39.5%, calorific values are 3947, 5927, 6334 kilocalories/kg, Fixed carbon 33.3%, 47.3%, 53.8%, bulk values are 435,373,403g/ml respectively. So finally, the charcoal made from causarina bark was selected due to low ash and high carbon values.

3.6 Treatment of composite effluent by Fly ash

The final composite effluent from (outlet effluent) 1 liter was treated with 0.5% fly ash followed by 0.2ml of 2% ferric alum was added as coagulant. The fly ash will adsorbs all the impurities present in the effluent such as carboxyl group etc., The pH found acidic and it is neutralized by 0.2mg neutral Na_2SO_4. The solution is filtered by Whatmann 42 paper and the filtrates were analyzed.

The color reduction found to be 83.3%, COD reduction found 41.5%, organics reduction found 56.6%, BOD reduction found 21.4%, TDS found almost unaltered with slight increase in total suspended solids values.

3.7 Treatment of composite effluent by Activated carbon

The final composite effluent from (outlet effluent) 1 liter effluent was treated with 1.0 g of non ferric alum and 1.0 g of charcoal up to pH 6.0. The supernatant solution was tested for the physico-chemical characteristics. The color found below the detection limit. The TDS reduction found 19.6%, COD reduction found 84.9% and BOD reduction found 85.7%. The total organics reduction found 80.3%. The results are displayed in Table 1. The study shows the treatment I and treatment II have the better efficiency in effluent treatment.

4.0 CONCLUSION:

The paper mill outlet effluents were collected characterized. The final composite effluent was treated with Ferric alum, Fly ash and neutral silicate has better color removing efficiency by 83.3% with total organics reduction 56.6% and COD reduction by 41.5% and BOD reduction by 21.4%. The final composite effluent was also treated with non-ferric alum and charcoal made from wood bark up to pH 6.0. The total dissolved solids reduction found 19.6%, COD reduction 84.9%, BOD reduction 85.7%, the total organic reduction found 80.3% and the effluent is colorless. It was concluded that the treatment of coagulation and adsorption will be cheaper and will fit as good tertiary treatment method. The drainage and disposal problem may be overcome by the selection of charcoal size. The precipitate obtained has lignin and charcoal which are easily combustible with high calorific values.

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